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PREPARATION OF EXPANDING OIL-WELL CEMENTS

The report substantiates the expediency of employment of expanding oil well cements for well cementing. It considers the principles of preparation of cements with different binding base and expanding additives. The mechanism of sulphoaluminate and oxide expansion is shown. It studies the effect of different factors on the expansion value and kinetics. It presents the results of experimental investigation and oil well cement compositions.

GENERAL PRINCIPLES

The problem of high-quality well cementing and formation isolation is one of the most crucial and complicated points in the whole cycle of the well construction. The presently used conventional materials cannot provide reliable sealing of the annular behind the casing string. It is caused by heightened water loss, low sedimentation stability, contraction and shrinkage strain during solidification. The above factors lead to formation of channels able to conduct formation fluid both along cement stone body and its contact zones (cement stone – formation, cement stone – casing string).

References [1, 2] show that portland cement stone solidified in the annulus as well as against low permeable formation has a worse bond with formation and casing as compared to the stone solidified in an interval of permeable and especially water-saturated formations. The formation of fluid conducting channels in the cement stone is also promoted by operations carried out inside the casing string. We have conducted calculations that show that the clearance forming between the cement stone and casing string can reach 1 mm depending on the value of pressure drop in the casing as well as on pipe type-size and material.

We consider that one of the promising directions to improve quality of well cementing sealing is employment of expanding oil-well cements that provide stress contact of the cement stone with the limiting surfaces. In our opinion the optimum expansion is 2 to 4% and contact pressure should be 2.5 to 3.0 MPa. Besides it is important to take a differential approach to kinetics of volumetric deformations of the cement stone. It is necessary that the main part of expansion should take place after pumping cement slurry into the annulus. Besides, the expansion should begin after the formation of the cement stone structure starts. If the expansion takes place during the cementing process when the suspension is in a liquid state it will not produce a positive effect on the quality of formation isolation. Too late expansion, i.e. after formation of rigid crystalline structure can cause fracturing and negatively effect the cement stone porosity. It is especially dangerous is there is possibility of free deformation. The cement stone solidification in a limited space, which is characteristic of wells, will

cause generation of stress contact with the limiting surfaces. In this case big inner stresses can appear decreasing the cement stone resistance to impact loads.

The foregoing proves the importance of making a correct cement composition to obtain the best quality of well cementing.

PREPARATION OF EXPANDING OIL-WELL CEMENTS

Preparation of expanding cements is based on introduction of additives forming new substances of a bigger volume when they interact with water or solidification products. To obtain the cement expansion crystalline pressures of calcium hydrosulphoaluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$ (three-sulphate form) or $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ (mono-sulphate form) are used. For this compound crystallization it is necessary that the solution should contain ions of Ca^{2+} , Al^{3+} , SO_4^{2-} and $\text{pH} > 12$. Gypsum and gypsum containing substances can be used as an expanding additive. It is possible to use a mixture of gypsum with high-alumina binder or high-alumina slag or anhydrous calcium sulphoaluminate. The resultant cements are quick-solidifying, have late expansion, work at the temperatures of 20 to 80 °C are employed in the construction industry.

Cements with oxide expansion are developed that are used for well cementing. Their expansion is provided due to formation of low soluble magnesium and calcium oxides that remained in the cement in a free state during clinker roasting. The high roasting temperature causes low chemical activity of the above oxides that is why at a temperature lower than 50 °C they hydrate slowly. It causes inner stresses after the cement stone has lost ability to plastic deformation. That is why the expansion is accompanied by fracturing and stone strength decrease. The hydration rate of CaO and MgO can be controlled due to the roasting temperature and dispersion degree of the additives. In this connection it is reasonable to prepare expanding cements with CaO and MgO by mixing portland cement with pre-roasted additives.

To prepare special cements chromate-aluminate additives are perspective. The expansion is provided by formation of high-chromate form of calcium hydroaluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$) and accompanied by increase of the solid phase by 4.6 times as compared to C_3AH_6 . According to this pattern the expansion of sulphaferrite cements takes place only due to formation of calcium hydrosulphaferrites. They differ in slowed-up structure formation at normal temperatures.

The expansion during solidification is characteristic of conventional portland oil-well cements mixed on mineralized liquids. The expansion is caused by negative contraction accompanied by crystallization of salts from the liquid during the stone solidification.

Generalizing it we can note that the expansion nature is in crystallization pressure of the solid phase that is not able to take its place in the porous space of the solidifying system. At the same time there is contradiction. The matter is that during hydration of all the clinker minerals the volume of solidification products increases as compared to the volume of the solid phase undergone the reaction. But even in this case the volume of the products providing expansion is less than pore volume formed in the

stone during full hydration of the cement. It means that possibility of expansion is determined by that extent to which the space previously occupied by the liquid phase will be filled with the solid phase.

The possibility of crystal intergrowth in pores is determined by relation of pore size and liquid phase oversaturation value. The condition of crystal growth is expressed by the equation

$$\ln\left(\frac{C}{C_0}\right) = \frac{2\sigma_{1,2} \cdot V_m}{RT \cdot r}, \quad (1)$$

since $\sigma_{1,2}$ - surface tension, V_m - molar volume, R - universal gas constant, T - temperature, r - pore radius.

It follows from this equation that crystalline hydrates of the expanding additive will intergrow in pores in the size of

$$r > \frac{2\sigma_{1,2} \cdot V_m}{RT \cdot \ln(C/C_0)}. \quad (2)$$

If oversaturation C/C_0 is constant, the smaller V_m the bigger probability of pore intergrowth with new crystalline hydrates. As noted before to provide the effective expansion to the expanding additive hydration it is necessary to form the frame of the solidifying cement. If the formed frame consists of pores with the radius corresponding to equation (2) the main part of expanding crystalline hydrates energy will be spent on filling pore volume and the expansion will not occur. It is necessary that growing crystals of the expanding additive should set against the cement stone frame. It follows from the equations that any expanding additive should have a certain corresponding size of solidifying cement stone pores. In other words, before the additive crystallization starts the pores of a corresponding size should form in the stone.

Under other equal conditions the pore size can be controlled by change of water-cement ratio, cement solidification rate.

Combined additives are promising that form crystalline hydrates of different molar volume. The same effect can be reached by mixing expanding cements with salt solutions that crystallize in pores earlier than expanding additives and decrease their size. Reagents slowing down the expanding additive hydration will also be effective for development of expanding cement compositions.

Thus, to prepare expanding cements with predetermined expansion value and to provide the desired pressure on the limiting surfaces it is necessary to control geometry of the basic binder in the initial period of solidification as well as quantity and rate of the expanding additive hydration.

CERTAIN FACTORS EFFECT ON THE CEMENT STONE EXPANSION

Slurry mixing time. Mixing of the cement with CaO additive during 3 hours which simulates cement slurry pumping into the well decreases the expansion stone value almost up to zero. Addition of MgO does not change the cement stone expansion

after the same treatment at the temperature of 80 °C. The temperature increase up to 120 °C combined with mixing decreased expansion by 15%. The cements of sulphoaluminate and sulphoferrite expansion did not change kinetics of the expansion during mixing at the normal temperature.

Ambient pressure and the stone stress state. This factor is of special importance for oil-well cements, since the cement stone works under conditions of all-round pressure. Besides, a significant role is played by the generated pressure kind. In case of mechanical load there is a critical value and when it is reached the cement stone expansion equals zero. In case of hydraulic pressure the expansion behavior changes. For cements with CaO additive the expansion reduced by 30% when pressure increased up to 50 MPa. The further pressure increase up to 100 MPa reduced the expansion even by 70%. For chromate aluminate cements the expansion reduced by 30% when the pressure increased from 10 up to 100 MPa and when these cements were mixed with NaCl it reduced by 25%.

During the expanding cement solidification in a closed space the crystalline pressure is spent for the irreversible change of separate stone structure elements and for the elastic deformation of the skeleton. It causes generation of the inner stress expressed as the expansion pressure. The stress generated by the expanding cement is directly proportional to its relative expansion value and to the cementing elasticity coefficient. When expansion limits are relieved, the stresses cause the elastic deformation of the skeleton. The latter is of great practical importance for compensation of the casing deformation during pressure decrease. The experiments have shown that the elastic deformation of the cement stone with CaO additive makes 4 to 5 % of the free expansion value at the pressure equal to 100 MPa. The higher pressure when the expanding cement solidification takes place, the bigger its elastic deformation.

To preserve stress contact the cement stone elastic deformation must be bigger than the casing deformation when pressure decreases inside it.

The analysis has shown that while the cement stone elasticity modulus grows its expansion must decrease. Especially intensive decrease takes place when elasticity modulus (E_{cs}) grows from $1 \cdot 10^4$ up to $5 \cdot 10^4$ Mpa. To obtain the desired contact pressure values we have determined the required values of the cement stone expansion depending on its elasticity modulus. For example, for the casing of 146 mm run into the well of 190 mm diameter we have obtained the following results (Table 1).

Table 1

E_{cs}, MPa	$1 \cdot 10^3$	$3 \cdot 10^3$	$3 \cdot 10^3$	$1 \cdot 10^4$
Expansion, %	1,8	1,1	0,7	0,2

They have shown that while the elasticity modulus grows the required contact stress can be reached with less expansion.

In order to generate the required contact stress without loss in the cement stone properties the maximum expansion must be reached in the initial period (hours) of solidification and then, while the elasticity modulus grows, the expansion rate and value must decrease in such a way that the generated inner stress should remain less than breaking strength of the cement stone structure bonds.

With the help of a specially designed apparatus we have determined contact stresses of different oil-well cements. It is shown that presence of the clay cake on the “cement – rock” interface sharply decreases the contact pressure for any cement type. It testifies to the necessity of a more strict approach to the well preparation for the casing running-in and cementing.

CONTROL OF BASE BINDER STRUCTURE-FORMING RATE

For any temperature conditions when expanding cements are used it is necessary that matrix structure-forming rate should be higher than additive crystallization rate.

When portland cement is used up to the temperature of 50 °C it is necessary to accelerate its solidification rate. Practically it is achieved due to employment of chemicals, increase of the binder specific surface, employment of solidification crystalline initiators, mechanic and chemical activation. The latter is realized with the help of the dsintegrator and has significant advantages as compared to other methods due to lower energy consumption and higher effectiveness.

The investigations have shown that during mechanic and chemical activation depending on the treatment conditions the solidification rate and the cement stone strength increase by 3 to 5 times. Besides, substances usually unable to solidify (slag, industrial waste) can show hydration activity. The disintegration technology allows optimization of the cement stone structure for conventional oil-well cements.

The picture shows the results of mercury porometry of the stone of the composition based on portland cement with calcium oxide expanding additive. As we can see the disintegrator technology of expanding cement preparation caused decrease of the stone integral porosity and simultaneous shift of the main pore volume in the direction of a less size.

NEW COMPOSITIONS OF EXPANDING CEMENTS

The experiments carried out with consideration of the above mentioned theoretical principles allowed us to develop several compositions of expanding cements. Calcium oxide obtained according to changed roasting technology is used as an expanding additive (D1, D2). The additive specific surface allowed optimization of expansion kinetics having coordinated it with the portland cement structure-forming rate. The results of the experiments are shown in Table 2. They show that the proposed materials have important advantages as compared to those employed before and can be recommended for well cementing.

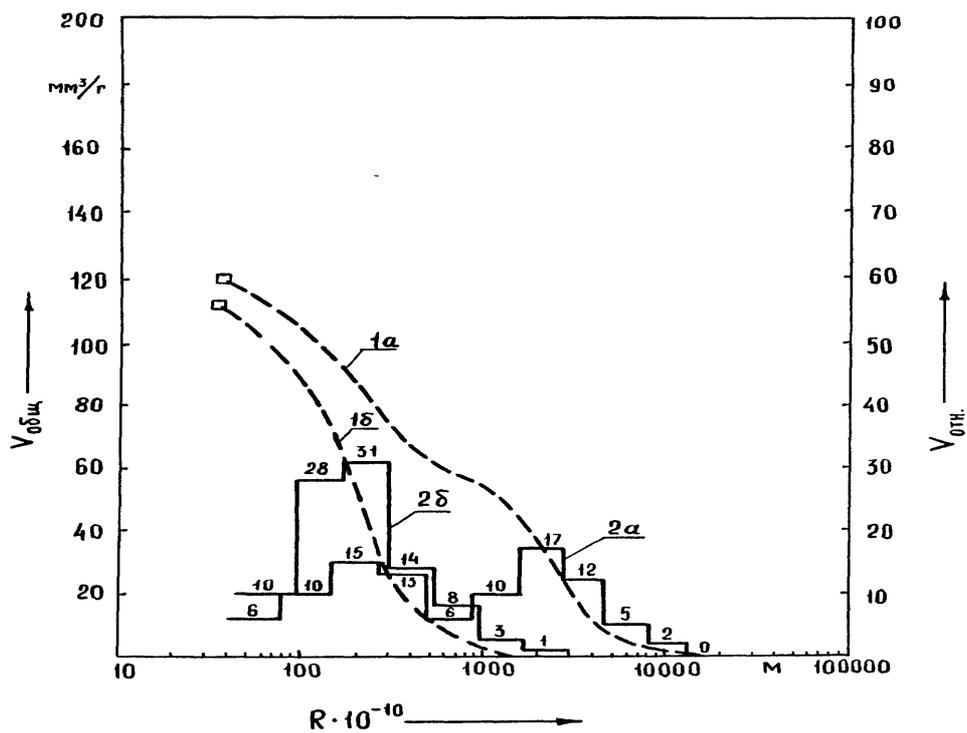
Table 2

Binder Composition	Mixing time, min	Expansion, %	Expansion Pressure, MPa	σ_{bend} , 2 days, MPa
Portland cement	3	-“-	1,82	2,61

Portland cement+3%D1	3	2,1	2,66	6,6
Portland cement+3%D1	60	0,88	4,07	10,3
Portland cement+3%D1 +0.2%LST	3	2,3	2,56	3,7
Portlandcement+3%D1 + 0.2%LST	60	0,5	5,06	2,28
Portland cement+3%D2	3	2,3	2	2,65
Portland cement+3%D2	60	1,7	2,8	3,8
Portland cement+3%D2 +0.2%LST	3	2,5	1,8	2,7
Portland cement+3%D2 + 0.2%LST	60	1,7	2,9	4,2

Note: = Water-cement ratio = 0.45; cement spreadability 20-21 cm;
LST – plasticizer.

Effect of Method of Oil-well Cement Composition Preparation on the Resultant Stone Structure (T = 22 °C)



1 – integral programme;

2 – differential programme;

a) – mechanical mixing of components;

b) – disintegration mixing of components

Fig.

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